

## EFFECTS OF A SURFACTANT ON THE MOTION OF A CONFINED GAS-LIQUID INTERFACE. THE INFLUENCE OF THE PECLET NUMBER

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**Abstract**— The displacement of a liquid initially contained in a capillary tube or between two closely spaced parallel plates by a gas phase, is largely affected by the presence of a soluble surfactant. The distribution of the surface active solute within the bulk and along the interface depends on the relative strength of convection, diffusion and the kinetics of adsorption/desorption. In this work, a complete description of the velocity and concentration fields in the bulk and along the interface is presented for several values of the Péclet number. The influence of this parameter on the film thickness is also analyzed.

**Keywords**— interfacial flow, surfactant, finite-elements, gas-liquid displacement.

### I. INTRODUCTION

The displacement of a gas-liquid interface between two closely spaced parallel plates or inside a capillary tube is a model widely used to analyze complex multiphase problems. Two interesting examples are the process of oil recovery by chemical flooding and the expansion dynamics that occurs during the opening of collapsed pulmonary airways. The simplest model of both processes is the motion of a semi-infinite bubble in a capillary tube initially filled with a viscous liquid, a problem that has received considerable attention since the pioneering work of Bretherton (1961).

An important issue of many multiphase systems is the role played by a surface active agent that is present either as an impurity or as an additive. The surfactant largely affects the dynamic behavior of a deforming interface. In fact, the adsorption of minor amounts of a surface active solute at a free surface reduces its surface tension and induces the appearance of interfacial tension gradients when the distribution of solute is not uniform. In the first example mentioned above, the injection of a surfactant solution helps to remobilize the residual oil from the porous rock by lowering the surface forces. In the second one, the occlusion may result from an insufficient biosynthesis of surfactants.

The influence of a surface active agent on the displacement of a confined gas-liquid interface, has been analyzed both analytically and numerically. Among the works that employ the first methodology, the more

comprehensive one is the study presented by Ratulowski and Chang (1988). These authors carried out an asymptotic analysis for both the hydrodynamics and the mass transfer problems and obtained solutions valid for very low motions and traces of surfactant. They detected five different cases depending on the relative magnitude of the transport mechanisms involved: bulk and surface diffusion, bulk and surface convection, and adsorption-desorption.

Other analytical works are those of Ginley and Radke (1988), Park (1992), and Stebe and Barthés-Biesel (1995). The former authors assumed that the concentration of surfactant in the bulk was uniform and that the interfacial concentration of surfactant was controlled by the kinetics of the adsorption-desorption process. Park, analyzed the case designated as diffusive-equilibrium model in Ratulowski and Chang's work. Finally, Stebe and Barthés-Biesel carried out an asymptotic analysis of the problem valid when the exchange of solute between the phase and the interface is controlled by the adsorption-desorption kinetic process. The main objective of all these analysis—valid when viscous forces are negligible compared to capillary forces—was to establish the influence of the surfactant on the film thickness left behind by the moving front.

One of the first numerical works dealing with the effects of a surface active agent on the displacement of a gas-liquid interface was published by Wassmuth *et al.* (1993). These authors studied the motion of the interface between parallel plates with and without a constriction using two different tessellations: a variable one for the free surface and a fixed one for the bulk phase. They presented solutions for a limited set of values of the dimensionless parameters that did not include the case of small Capillary number.

Very recently, Ghadiali and Gaver (2003) used a computational model of a semi-infinite bubble moving in capillary tube filled with a surfactant solution. They showed results for the free surface shape, the flow field, the concentration profiles and the pressure drop as a function of the dimensionless parameters of the system. The range of Capillary number considered was 0.015-10

and the interfacial Péclet number was  $10^3$  in all the solutions reported.

In a previous work (Severino *et al.*, 2003), we numerically studied the influence of a soluble surfactant on the displacement of a gas-liquid interface moving between parallel plates. The complete set of governing equations with their appropriate boundary conditions was solved using the finite element method combined with a suitable parameterization of the free surface. The main goal of that work was to predict the film thickness as a function of the relevant dimensionless numbers of the system. The numerical technique produced solutions at very low values of the Capillary number that were in excellent agreement with those computed with the asymptotic model presented by Ratulowski and Chang.

Although the two last cited articles present a comprehensive analysis of the problem, none of them is exclusively focused on the effects of the Péclet number. Taking into account that the distribution of surfactant in the bulk and along the interface should be largely affected by the magnitudes of both the bulk and surface Péclet numbers, it is interesting to analyze the gas-liquid displacement in situations characterized by different values of these parameters. This is indeed the objective of this work.

## II. MATHEMATICAL FORMULATION AND NUMERICAL TECHNIQUE

### A. The governing equations

We consider the steady motion of a semi-infinite inviscid bubble between parallel plates and in a capillary tube, which displaces a Newtonian liquid of viscosity  $\mu$  and density  $\rho$ . The speed of the bubble is  $U$  and its pressure is uniform everywhere; therefore, the gas phase exerts only normal stresses on the interface. The pressure of the gas is taken as the reference pressure of the system and it is arbitrarily set equal to zero.

The radius of the tube ( $d$ ) or the distance between the plates ( $2d$ ) is small enough to neglect the effect of gravity.

We assume that surfactant molecules are present at the interface as well as in the bulk phase, their distribution depending upon convection and diffusion. The concentration of solute in the liquid far away from the meniscus is uniform and equal to  $C_N$ .

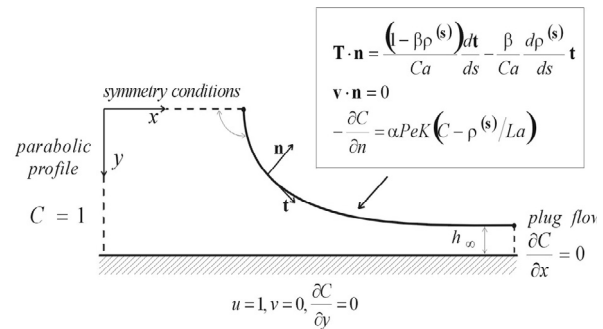
Then, the dimensionless governing equations are Navier-Stokes, continuity and the mass balance of the surfactant,

$$Re \nabla \cdot (\mathbf{v}\mathbf{v}) - \nabla \cdot \mathbf{T} = \mathbf{0}, \quad \mathbf{T} = -p\mathbf{I} + \nabla \mathbf{v} + (\nabla \mathbf{v})^T, \quad (1)$$

$$\nabla \cdot \mathbf{v} = 0, \quad (2)$$

$$Pe \nabla \cdot (C\mathbf{v}) = \nabla^2 C. \quad (3)$$

The scales employed are  $U$  for velocities,  $d$  for lengths,  $\mu U/d$  for pressures and stresses, and  $C_N$  for the bulk concentration of the surfactant. In Eq. (1),  $Re = \rho U d / \mu$  is the Reynolds number and in Eq. (3),  $Pe = U d / D$  is the bulk Péclet number,  $D$  being the diffusion coefficient of the solute in the liquid phase.



**Figure 1.** Schematic representation of the problem and coordinate system adopted.

The coordinate system adopted moves with the gas phase at velocity  $U$  (see Fig. 1). Then, the conditions to be imposed at the boundaries of the domain are those shown in Fig. 1. We assume that the solid walls are impermeable and the liquid adheres there. The center line of the tube (or the plane located amidst the plates) is a symmetry line (plane). The flow is unidirectional and the concentration of surfactant is uniform far upstream and far downstream from the meniscus. Moreover, in this last region the free surface becomes parallel to the solid wall and the thickness of the liquid film becomes equal to  $h_N$ ; also, the concentration of surfactant in the bulk and at the interface should approach equilibrium.

To establish the boundary conditions at the interface, we presume that the free surface is Newtonian and inviscid; consequently, the surface stress tensor is  $\mathbf{T}^{(s)} = \sigma(\mathbf{I} - \mathbf{nn})$ , where  $\mathbf{I}$  is the identity tensor,  $\mathbf{n}$  is the unit vector normal to the interface, and  $\sigma$  is the gas-liquid surface tension which depends on the local concentration of surfactant adsorbed at the interface ( $\Gamma$ ). Thus, the balance of stresses at the interface results

$$\mathbf{T} \cdot \mathbf{n} = \frac{d}{ds} \left( \frac{\bar{\sigma}}{Ca} \right) \mathbf{t}, \quad \bar{\sigma} = \frac{\sigma}{\sigma_M}, \quad (4)$$

where  $Ca = \mu U / \sigma_M$  is the capillary number defined with the value of the surface tension corresponding to a "clean" interface ( $\sigma_M$ ), and  $\mathbf{t}$  is the unit vector tangent to the free surface pointing in the direction of increasing arc-length,  $s$ . It is easy to see that if there are not surfactants adsorbed at the interface, Eq. (4) will simplify to the boundary condition usually imposed at the free surface.

In order to evaluate expression (4), a relationship between  $\bar{\sigma}$  and the local concentration of surfactant is needed; in this work we adopt the following equation that is a linearized form of Frumkin equation valid when the concentration of surfactant adsorbed is much smaller than the maximum realizable concentration of solute  $\Gamma_N$ ,

$$\bar{\sigma} = 1 - \beta \rho^{(s)}. \quad (5)$$

In Eq. (5),  $\beta = RT\Gamma_N/\sigma_M$  is the elasticity number,  $R$  being the universal gas law constant and  $T$  the temperature of the system,  $\rho^{(s)}$  is the concentration of surfactant measured in units of  $\Gamma_N$ .

The interface is a material surface, then the kinematic condition applies,

$$\mathbf{v} \cdot \mathbf{n} = 0. \quad (6)$$

We assume that the solute adsorbs/desorbs at/from the interface following first order kinetic laws. Thus, we have

$$-(\nabla C \cdot \mathbf{n})_{FS} = \alpha PeK \left( C_{FS} - \frac{\rho^{(s)}}{La} \right). \quad (7)$$

Equation (7) can be derived from Langmuir's law assuming that the concentration of adsorbed surfactant is much lower than the maximum concentration realizable (see, e.g. Edward *et al.*, 1991). In expression (7)  $C_{FS}$  is the concentration of surfactant in the bulk near the interface,  $\alpha = k_a C_N d/U$  is the Hatta number,  $La = k_a C_N/k_d$  is the Langmuir number, and  $K = \Gamma_N/C_N d$ ;  $k_a$  and  $k_d$  being the adsorption and desorption rate constants, respectively.

In order to evaluate Eqs. (5) and (7) we must employ the interfacial mass balance of solute from which the interfacial concentration of surfactant should be determined. We assume that interfacial convection and interfacial diffusion distribute the net flux of surfactant that exists between the bulk phase and the interface; then, we have

$$Pe_S \nabla_S \cdot (\rho^{(s)} \mathbf{W}) - \nabla_S^2 \rho^{(s)} = -\alpha Pe_S \left( C_{FS} - \frac{\rho^{(s)}}{La} \right), \quad (8)$$

where  $\nabla_S$  is the surface counterpart of  $\nabla$ ,  $\mathbf{W} = \mathbf{W}\mathbf{t}$  is the surface velocity and  $Pe_S = Ud/D_S$  is the interfacial Péclet number;  $D_S$  being the surface diffusion coefficient of the surface active agent. Considering that  $D_S$  is of the same order of magnitude than  $D$  (Agrawal and Neumann, 1988), in this work we will usually take  $Pe = Pe_S$ ; nonetheless, on occasions we will employ values of  $Pe_S$  ten times larger than  $Pe$  to assess the effect of interfacial diffusion.

Equation (8) requires boundary conditions; we impose  $\partial \rho^{(s)}/\partial s = 0$  at both ends of the interface, at the

tip of the bubble ( $s = 0$ ) due to symmetry, and at the point where the free surface intercepts the outflow plane due to the existing equilibrium between the bulk and the interface.

The remaining boundary conditions to be satisfied at the interface establish that the free surface is parallel to the solid wall at the outflow plane and that the angle formed by free surface and the center line (symmetry plane) is equal to  $\pi/2$ .

## B. The numerical method

The set of governing equations and boundary conditions was solved numerically using the finite element method. A detailed description of the numerical technique employed can be found in Severino (2001); therefore, in the following paragraphs we briefly describe its main features.

We used quadrilateral elements to tessellate the flow domain. The elements located near the free surface have two sides that are straight lines while the shape of the remaining sides depend on the free surface shape. Each element is isoparametrically mapped onto the unit square by means of nine-node biquadratic basis functions. In this way the computational domain is built, the interface being represented by a coordinate line.

The velocities and the bulk concentration of surfactant are interpolated using biquadratic basis functions, while the pressure is interpolated using continuous bilinear basis functions. The interfacial quantities, which are the coefficients that locate the free surface and the interfacial concentration of solute, are interpolated using the one dimensional specialization of the biquadratic basis functions. The residuals are built in the usual form and in this way a set of nonlinear ordinary equations is obtained. This set is solved by Newton's method, the iterative process being stopped when the norm of the difference between two successive iterations is equal to or smaller than  $10^{-6}$ .

The main objective of this work is to describe the effect of the Péclet number on the dynamics of the interfacial displacement. Therefore, a good representation of every field variable at the interface and in its vicinity is relevant. The number of elements and its distribution in the finite element mesh used to solve the problem was established according to the following criteria:

- The values of the interfacial variables should not be affected by further refinements.
- The outflow plane should be located far enough downstream ( $x_F$ ) so that the slope of the free surface and the concentration of solute at this point are almost insensitive to variations in  $x_F$ .

From the numerical tests performed, we concluded that a mesh having 260 elements, with 151 nodes located along the free surface suits the above requirements. A significant feature of the mesh is the location

of an infinite element at  $x=0$ , which is used to eliminate the oscillations associated to large values of the Péclet number and to correctly impose the concentration boundary condition there.

### III. NUMERICAL SOLUTIONS

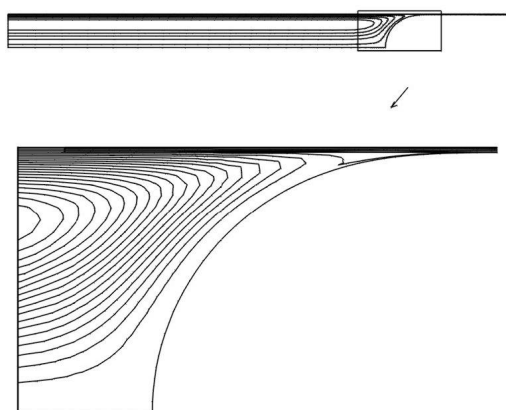
In order to focus our study on the influence of the Péclet number on the dynamics of the gas-liquid displacement, we have restricted our analysis just to systems characterized by  $Re = 0$ ,  $Ca = 0.001$ ,  $La = 1$ ,  $K = 1$ ,  $\alpha = 0.05$ ,  $\beta = 0.2$ , —values that will be kept unchanged throughout this work— and several values of  $Pe$  and  $Pe_S$ . Solutions were obtained for both the plane and the axisymmetric geometries. A close inspection of these solutions shows that the results are quite insensitive to the geometry; consequently, in the next section we discuss predictions pertaining to the axisymmetric case only.

Results to be presented in this Section are organized as follows. First, the flow fields and the concentration of surfactant in the bulk are analyzed, then, the distribution of the interfacial variables along the interface are discussed, and finally the thickness of the liquid layer left behind by the moving front as a function of  $Pe$  is reported.

#### A. Flow fields and the distribution of surfactant in the bulk

In this Subsection we present the velocity fields and the isoconcentration lines for values of the Péclet number ranging between 0.1 and 1000.

The streamlines are almost insensitive to variations of  $Pe$  in the range just stated; thus, the streamlines illustrated in Fig. 2 for  $Pe = Pe_S = 100$ , can be taken as representative of all the cases studied.



**Figure 2.** Streamlines for  $Pe = Pe_S = 100$ . Axisymmetric case.

The flow field presents two regions: one located ahead of the meniscus, where the fluid recirculates, and

another situated close to the solid walls that ends in the thin film formed far away from the bubble front. This flow pattern is present when the dimensionless thickness of the film left behind by the moving front ( $h_N$ ) satisfies the following conditions:  $h_N < 1/3$  in the planar case, and  $(1 - h_\infty)^2 > 1/2$  in the axisymmetric case, (see Giavedoni and Saita, 1997), a situation that is verified for  $Ca = 0.001$ . In the swirl the solute is convected toward the interface by the fluid that is near the solid wall and back to  $x = 0$  by the fluid that is moving closer to the center of the tube.

The predictions obtained for the distribution of surfactant in the bulk phase are summarized in Fig. 3. There, the results are shown as a function of the Péclet number, which measures the relative strength between convection and diffusion, and they are ordered from top to bottom for decreasing diffusive effects. The predictions presented in Fig. 3 (a) indicate that diffusion is really important when  $Pe = 1$ ; in fact, one may observe that the isoconcentration lines, being almost perpendicular to the tube walls, hardly reflect any fluid motion. In other words, the fluid motion practically does not affect the distribution of solute.

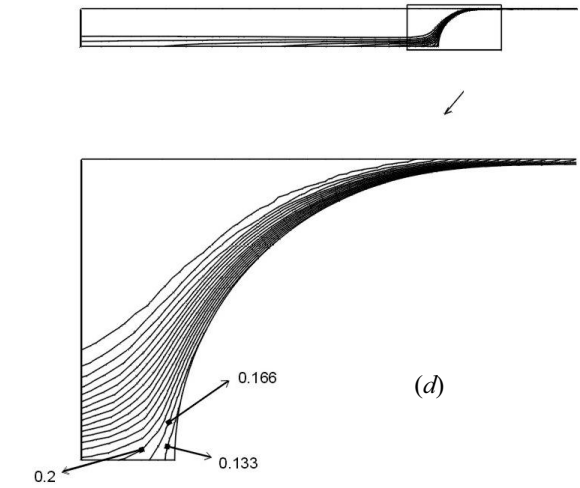
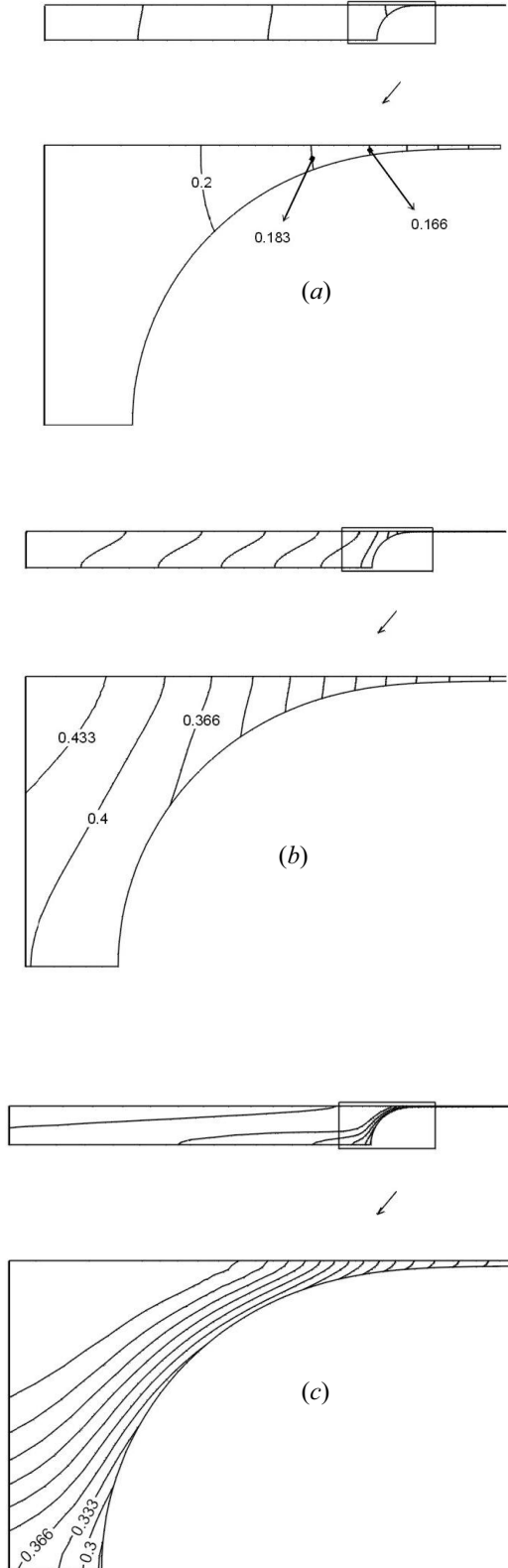
The features just described start to change as soon as the diffusive effects weaken. Figure 3 (b) portrays the results for  $Pe = 10$  showing that the isoconcentration are much closer than for  $Pe = 1$  (notice the new spacing), and that they begin to adopt an S shape. These changes indicate the relative strengthening of convection.

When convection is the most important mechanism of mass transfer, the isoconcentration lines strongly depend on the flow field; thus, one should expect these lines to become almost parallel to the streamlines as the Péclet number is augmented. Our numerical solutions show that this is indeed the case when the isoconcentration lines for  $Pe = 1000$  (Fig. 3 (d)) are compared with Fig. 2.

The inspection of the sequence of isoconcentration lines depicted in Fig. 3 establishes that the distance between two consecutive lines decreases as the Péclet number is increased, as expected. The bulk phase is richer in surfactant for larger values of  $Pe$ , except in the immediate vicinity of the interface as we discuss in B. In fact, as the convective transport becomes more intense the surfactant is more easily transported from the entrance region towards the meniscus zone; therefore, when  $Pe \gg 1$  the concentration gradients are important near the free surface only.

The isoconcentration lines for both planar and axisymmetric cases look quite alike; the only meaningful difference seems to be that cylindrical geometry favors convective effects better than the planar one. Therefore, the liquid in the bulk near the meniscus is richer in surfactant when the displacement takes place in a capillary tube.

Results presented above show that the isoconcentration lines strongly depend on the value of the Péclet number. Next, we discuss the effects of this parameter on the interfacial variables.



**Figure 3.** Isoconcentration lines for the axisymmetric case; (a):  $Pe = 1$ , (b):  $Pe = 10$ , (c):  $Pe = 100$  and (d):  $Pe = 1000$ . In all cases  $Pe = Pe_s$  and the difference between two consecutive lines is equal to  $0.1/3$ , except for case (a) where this last value is halved.

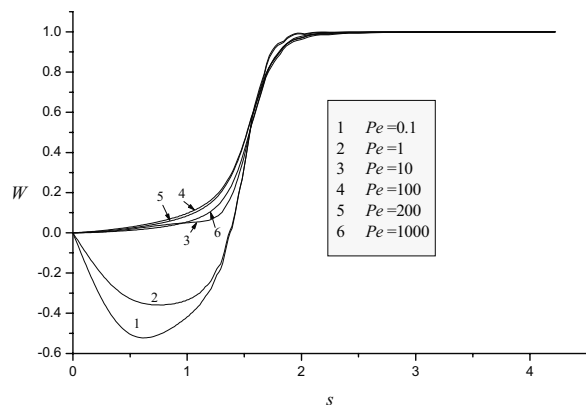
## B. The interfacial variables

It is interesting to analyze how the interfacial variables change with Péclet number. In Figs 4-7 we illustrate the interfacial velocity ( $W$ ), the concentration of solute in the bulk near the interface ( $C_{FS}$ ) and at the free surface ( $\rho^{(S)}$ ), and the tangential component of the interfacial traction vector for some values of the Péclet number considered in this work. The results depicted in these figures are for the axisymmetric case.

For  $Ca=0.001$ , and in a system free of surfactant, the recirculating flow that exists in the liquid ahead the meniscus gives rise to an interfacial stagnation ring located near the solid wall (Giavedoni and Saita, 1997). Therefore, the interfacial velocity along  $s$  results negative between this stagnation ring and the tip of the bubble, and positive elsewhere. Any inert solute adsorbed at the interface will be convected from the stagnation ring toward the bubble tip or toward the film region; consequently, one should expect a maximum concentration of solute at the bubble vertex and a depleted zone near the stagnation line. If the solute is a surface active agent, the concentration gradient so generated will give rise to a non zero surface traction. This traction will try to restore a uniform concentration of surfactant inducing significant changes in the magnitude of the interfacial velocity as it is illustrated in Fig.4.

When  $Pe$  is small, diffusion evens the interfacial concentration of solute; thus, the concentration gradients are negligible and the interfacial velocity is slightly affected. This is precisely the case of  $Pe = 0.1$  depicted in Fig. 4 where the magnitude of  $W$  between the two stagnation points is just smaller than for a clean system. As the Péclet number is increased, the stagnation ring displaces toward the bubble tip and consequently, the

extension of the region in which  $W$  is negative shortens. When the two stagnation points merge at  $s = 0$ , the region in which  $W$  is negative disappears. Thus, the recirculating flow is detached from the interface, and there is a very thin region between the swirl and the free surface where the liquid velocities are very small.



**Figure 4.** Free surface velocity for selected values of the Péclet number. Axisymmetric case.

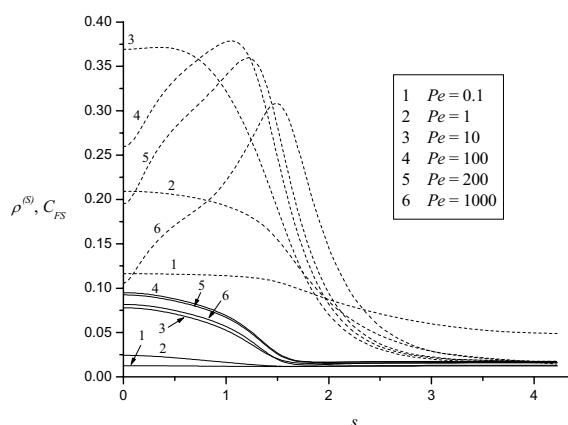
An interesting feature of the curves illustrated in Fig. 4 is the following. For values of  $Pe$  smaller than or equal to 100, the interfacial velocity increases with this parameter, while for Péclet larger than 100,  $W$  diminishes in the region that is approximately delimited by the two stagnation points in the clean system. This behavior is related to the changes produced in the gradients of interfacial concentration of solute, which can be easily envisaged through the curves of  $\rho^{(s)}$  shown in Fig. 5. However, before scrutinizing the curves there portrayed it would be advantageous to have a mental picture of the main phenomena occurring in the system we are studying.

The case under analysis is the particular one already defined and the only variable we are changing is the strength of the diffusive effects; i.e. the Péclet number. Though the solute is transported by convection and diffusion in both the bulk and the interface, diffusion is the ultimate mechanism that transfers surfactant to the thin liquid layer adjacent to the interface where the adsorption/desorption process takes place (see Eq. (7)). The diffusive process is hindered when  $Pe$  is large; i.e. a kind of barrier is raised restricting the passage of solute. Therefore, the surfactant in the bulk builds up near the meniscus and larger concentration gradients arise as  $Pe$  is augmented; this feature is clearly depicted by the iso-concentration lines which become closely packed near the interface (see Figs. 3 (c), (d)). On the other hand, when  $Pe$  is small the diffusive effects are strong and there is no restriction for the solute to be transferred. For the same reason, weak concentration gradients are observed at the interface and in the adjacent liquid (Fig.5, curves 1 and 2); also the effects of interfacial

adsorption are transmitted by diffusion, and they are perceived well far ahead of the bubble front (Fig. 3 (a)).

Figure 5 shows how the concentration of solute changes at the interface—and in the liquid bulk close to it—when Péclet number is varied. When  $Pe$  is small (0.1 or 1)  $C_{FS}$  and  $\rho^{(s)}$  behave similarly: they decay very slowly from their maximum values at the bubble tip toward the film region; consequently, the equilibrium between the bulk and the free surface is achieved far away from the meniscus.

When Péclet number is increased, the interfacial concentration of solute along the meniscus also increases because the interfacial diffusive transport toward the film region is less effective. Therefore, the curves of  $\rho^{(s)}$  in Fig. 5 present a more noticeable maximum while the concentration in the film left behind by the bubble slightly changes. Nevertheless, the distribution of surfactant at the meniscus presents a non monotonic behavior: it increases between  $Pe$  0.1 and 100, and it decreases for values of  $Pe$  above 100. A similar non-monotonic behavior was previously reported for the surface velocity.



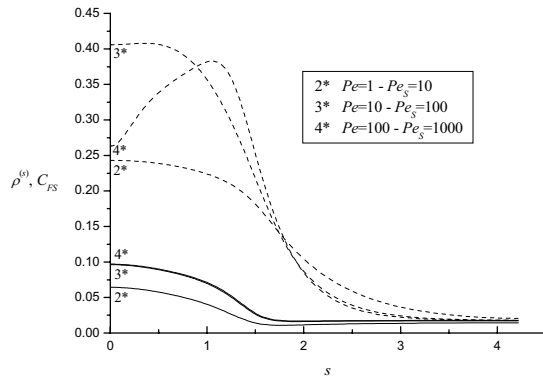
**Figure 5.** Concentration of surfactant at the interface (—) and in the liquid adjacent to the interface (----), for selected values of the Péclet number. Axisymmetric case.

The concentration of solute near the interface ( $C_{FS}$ ) follows the changes of  $\rho^{(s)}$  and also increases in the meniscus region with  $Pe$ . However, for  $Pe=10$  the maximum of  $C_{FS}$  is not located at the tip of the bubble any longer. This fact is more clearly observed in the curves corresponding to  $Pe$  equal 100, 200 and 1000, where the maximum not only displaces toward the film region but it also diminishes as the Péclet number increases. It appears that diffusive effects have become so weak that they can not overcome the action of convection, which in the bulk phase rapidly diminishes the amount of surfactant available in the bubble cap region (cf. Figs. 3 (c), (d)). This reduction induces, in turn, the smaller

values presented by  $\rho^{(s)}$  at the meniscus as the Péclet number is augmented beyond 100 (curves 4-6 in Fig. 5).

The gradients of interfacial concentration are more interesting to analyze since they are directly related to the interfacial forces that will produce variations not only in the interfacial velocity, but also in the thickness of the film deposited by the moving bubble. For the case under analysis Fig. 5 indicates that the curves of  $\rho^{(s)}$  for  $Pe$  1, 10 and 100 are representative of small, intermediate and large gradients of interfacial concentration of solute, respectively. In the previous paragraphs, we pointed out that these changes are mainly originated in the interfacial diffusive transport that becomes less effective as  $Pe$  increases. In order to verify this assertion we have computed solutions for values of  $Pe$  equal to 1, 10 and 100 as before, but now we have considered an interfacial Péclet ( $Pe_S$ ) ten times larger than  $Pe$ . The curves labeled 2\*, 3\*, and 4\* in Fig. 6 portray the corresponding computed predictions and they should be compared with curves 2, 3, and 4 of Fig. 5.

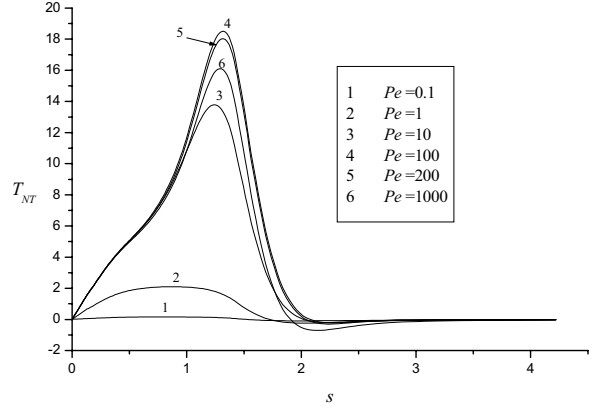
The curves of interfacial concentration as well as the curves of concentration in the adjacent liquid, move toward higher values in the meniscus region. The interfacial concentrations considerably augment for  $Pe = 1$ , the increments are less noticeable for  $Pe = 10$  and they are almost negligible for  $Pe = 100$ . Since the interfacial concentration in the film region ( $s \geq 2.5$ ) remains unchanged, we conclude that gradients of interfacial concentration along the meniscus vary significantly and so does the tangential component of the surface traction.



**Figure 6.** Concentration of surfactant at the interface (—) and in the liquid adjacent to the interface (----), for  $Pe_S = 10 Pe$ .

In Fig. 7 we illustrate the tangential component of the surface traction for the curves of  $\rho^{(s)}$  presented in Fig. 5.  $T_{NT}$  is almost zero for  $Pe = 0.1$  in agreement with the nearly uniform distribution of surfactant along the interface. For larger  $Pe$ , the value of  $T_{NT}$  presents a maximum that is located ahead of the point at which the concentration of solute is minimum, and it decays to zero in the film region where phase-interface equilib-

rium is finally attained. If the values of  $T_{NT}$  corresponding to the results of Fig. 6 were included in Fig. 7 curve 2\* would reach a maximum value of 12 while curves 3\* and 4\* would reach 20.7 and 21, respectively.

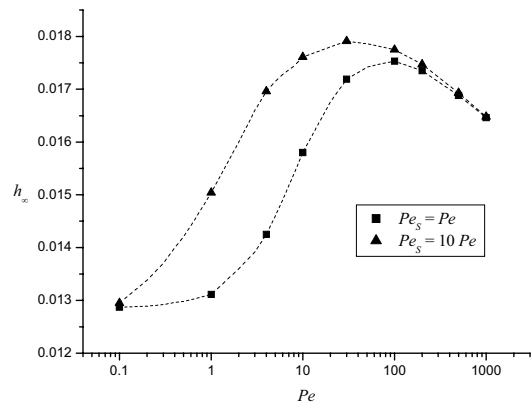


**Figure 7.** Tangential component of the surface traction pertaining to the curves of interfacial concentration shown in Fig. 5.

### C. The film thickness

The thickness of the film left behind by the moving bubble is one of the most interesting results to be obtained because of its practical implications.

Figure 8 presents the values of film thickness predicted versus the bulk Péclet number ( $Pe$ ); one set of results pertains to the cases of  $Pe_S = Pe$  and the other to the cases of  $Pe_S = 10Pe$ . In both instances the trend followed by the film thickness depends on the Marangoni traction ( $T_{NT}$ ).



**Figure 8.** Film thickness versus  $Pe$ ; curve (a):  $Pe_S = Pe$ , curve (b):  $Pe_S = 10Pe$ .

When  $Pe_S = Pe = 0.1$  the tangential component of the surface traction is nearly zero along the whole surface, therefore, the film thicknesses of the contaminated and the clean systems are practically equal. For larger values of  $Pe$ , results reported in Fig. 7 show that the Marangoni traction is positive except in a very small region of the free surface; therefore, more liquid will be pulled toward the film region and the film formed will be thicker than in the non surfactant case. Nevertheless, the surface traction does not increase monotonically with  $Pe$  and, consequently, the thickness of the film presents a maximum near  $Pe=100$ .

When  $Pe_S = 10Pe$  the system behaves rather similarly to the case just described; that is the film thickness increases from values pertaining to the corresponding clean system and, after reaching a maximum when  $Pe$  is about 30, decreases and the curve approaches the thickness values obtained before. The most remarkable difference with the previous results is the location of the maximum that has shifted toward lower values of  $Pe$  as expected.

The non-monotonic behavior of the film thickness is a direct consequence of the non-monotonic behavior presented by the interfacial concentration of solute, which was already explained when the features of the results depicted in Fig. 5 were discussed. At low values of  $Pe$  (more precisely low values of  $Pe_S$ ) both  $\rho^{(s)}$  and its gradient increase when the interfacial diffusive effect becomes weaker; in turn, a larger interfacial concentration gradient produces a thicker film. However, a point is reached where the diffusive effects are weak enough so that convection takes control; in this situation the liquid adjacent to the meniscus is depleted of solute by convection. This event also reduces the interfacial concentration of surfactant and its gradient and, as a consequence, the thickness of the film diminishes. In summary, the changes in film thickness are related to the different mechanisms of mass transfer prevailing in different regions of Péclet values.

#### IV. CONCLUSIONS

In this work a comprehensive description of the effects of the Péclet number on the distribution of surfactant in the bulk and along the interface of a moving bubble was presented. The problem was analyzed when the displacement of the liquid by the gas phase takes place either between parallel plates or in a capillary tube. The results obtained in both geometries are almost identical.

It is shown that the interfacial concentration of surfactant in the meniscus presents a non monotonic behavior: first it increases as  $Pe$  is augmented but then further increments of this parameter give rise to a lower and more uniform distribution of the surface active solute. The value of  $Pe$  at which the maximum concentration is achieved depends on the magnitude of surface diffusion. The non monotonic behavior observed in the interfacial

distribution of surfactant is responsible for the maximum detected in the film thickness.

#### Acknowledgments

This research was supported by CONICET, Universidad Nacional del Litoral and ANPCyT.

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Received: August 10, 2004.

Accepted: November 4, 2004.

Recommended by Subject Editor Gregorio Meira.